PATENT SPECIFICATION (11) 1242895

DRAWINGS ATTACHED

1242895

(21) Application No. 42949/68 (22) Filed 10 Sept. 1968

(31) Convention Application No. 669933 (32) Filed 22 Sept. 1967 in

(33) United States of America (US)

(45) Complete Specification published 18 Aug. 1971

(51) International Classification C 09 b 48/0

(52) Index at acceptance C4P D1C

(54) OXIDATION OF 6,13-DIHYDROQUINACRIDONES

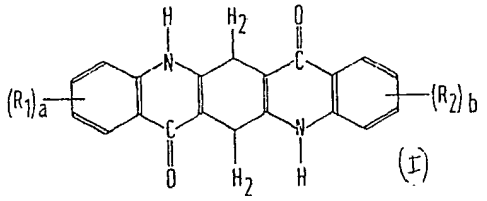
(71) We, E. I. Du Pont De Nemours and Company, a corporation organised and existing under the laws of the State of Delaware, United States of America, of Wilmington, State of Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the oxidation of 6,13-dihydroquinacridone compounds (DQA) in aqueous medium to mixtures of the corresponding linear quinacridone (QA) and quinacridonequinone (QAQ).

The oxidation of DQA to linear quinacridone (QA) in alkaline medium with an oxidant such as sodium meta-nitrobenzenesulfonate (SNBS) is disclosed in U.S. Patent Nos. 2,821,529, 2,844,484, 2,969,366, 3,007,930 and 3,009,916. The medium in which these reactions are commonly conducted consists of a mixture of water and a water soluble alcohol, and it is possible by controlling the ratios and concentrations of the various components in the system to obtain the QA in the desired crystal phase. The presence of a water soluble alcohol in the system precludes the formation of any QAQ in significant amounts.

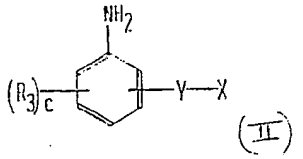
U.S. Patent No. 3,148,075 describes a method of oxidizing DQA to a mixture of QA and QAQ utilizing similar types of oxidants, the essential difference between the process of this patent and that of its predecessors being that the oxidation is conducted in an essentially aqueous medium at a pH above 13. However, a small amount of an organic liquid in the reaction medium which may facilitate the production of solid solutions is permissible (Col. 3, lines 27—33, inclusive). The patent lists permissible organic liquids which are useful for this purpose (Col. 3, lines 34—40, inclusive) but warns that "the amount of organic liquid should be kept very low . . . " and that "the use of larger amounts of such liquid in the reaction results in a linear quinacridone product rather than a mixture of quinacridone and quinacridonequinone" (Col. 3, lines 40—46). Actually, the highest ratio of QAQ/QA attainable by the method described in U.S. Patent No. 3,148,075 is of the order of 35/65, the remainder being QA. The patent does not suggest any modification of the procedure which might lead to significantly higher proportions of QAQ.

We have now discovered a process for oxidizing DQA compounds in alkaline medium which results in high proportions of the corresponding QAQ compound. According to the present invention we provide a process for preparing a mixture of a quinacridonequinone and a quinacridone which comprises oxidizing, in an alkaline medium, a corresponding dihydroquinacridone of the general formula



(I)

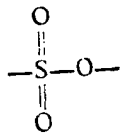
wherein R_1 and R_2, which may the same or different, are a halogen atom, an alkyl group of from 1 to 3 carbon atoms, or an alkoxy group of from 1 to 3 carbon atoms, and a and b, which may be the same or different, are 0, 1, or 2, in the presence of a compound of the formula



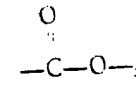
(II)

[*Price 25p*]

wherein R_3 is as defined above for R_1 and R_2, c is 0, 1, 3, or 4, —Y— is the group



or



and —X is sodium or potassium.

In formula I, the R_1 and R_2 groups are preferably symmetrically arranged. In formula II, R_3 is preferably a single replacement of hydrogen on a nuclear carbon atom (i.e. c is preferably 1).

The Drawing

The drawing is a plot of the weight percentages of quinacridone (solid line) and quinacridonequinone (broken line) as ordinates against the mol ratio of oxidizing agent/formula II compound present during the oxidation, as abscissa.

While the process of the present invention has been exemplified in the following examples with SNBS as oxidizing agent, other oxidizing agents may be used such as nitrobenzene, *p*-nitrotoluene, *m*-nitrophenol, *p*-nitrobenzoic acid, *m*-nitrobenzoic acid, 4-nitrophthalic acid, and sodium 2-methyl-5-nitro-benzenesulfonate.

The dihydroquinacridones that may be oxidized by this procedure as defined in Formula (I) include unsubstituted dihydroquinacridone, as well as both symmetrically and unsymmetrically substituted dihydroquinacridones. Examples of such substituted dihydroquinacridones are 2,9-dimethyl-6,13-dihydroquinacridone, 2,9-difluoro-6,13-dihydroquinacridone, 2,9-dichloro-6,13-dihydroquinacridone, 4,11-dichloro-6,13-dihydroquinacridone, 4,11-dimethyl-6,13-dihydroquinacridone, 2,9-dimethoxy-6,13-dihydroquinacridone, and 4-chloro-6,13-dihydroquinacridone. The substituted dihydroquinacridones produce both a substituted quinacridone and a substituted quinacridonequinone, wherein the substituents are in the same relative positions respectively as they are in the starting material.

The amount of oxidizing agent used may vary over a wide range. As little as 1 mole of the oxidizing agent per mole of dihydroquinacridone will convert the dihydrocompound to a mixture of quinacridone and quinacridonequinone. The upper range is determined solely by economic considerations. It is preferred to use 1 to 2 moles of oxidizing agent per mole of dihydroquinacridone. Since most dihydroquinacridone compounds show characteristic fluorescence under ultraviolet light, this property may be used to advantage to determine the reaction time. The reaction is usually conducted until no fluorescence is detectable. Reaction times of 3 to 6 hours are usually sufficient, but the time required will depend to some extent upon the temperature and the nature of the particular dihydro-derivative to be oxidized. In general, longer reaction times have no adverse effect on the reaction products.

As shown in the following Examples, the product may be obtained under conditions which will lead to a mixture of a linear quinacridone and a quinacridonequinone or to a solid solution of these two components where one compound enters into the crystal lattice of the other. It is also possible to obtain a composition comprising a physical admixture of a solid solution with either a quinacridone or a quinacridonequinone, or with both of these. In addition to sodium metanilate (SMA) and sodium sulfanilate, aniline derivatives as defined by Formula II above may be used to direct the oxidation reaction and promote the formation of higher proportions of the quinacridonequinone in the oxidation of a dihydroquinacridone. Substituents, R_3, which promote the solubilization in an aqueous alkaline solution are particularly desirable. Typical suitable agents include pottasium metanilate, sodium 3-amino-5-chloro-benzenesulfonate, sodium 3-amino-5-methyl-benzenesulfonate, sodium 3-amino-5-ethoxy-benzenesulfonate, potassium sulfanilate, sodium orthanilate, sodium anthranilate, sodium *m*-aminobenzoate, and sodium *p*-aminobenzoate.

The products of the process of the present invention are useful as pigments.

In the Examples which follow, the ratio of QAQ to QA in the product is determined spectrophotometrically in sulfuric acid solution. For this purpose it has been found advantageous to use the absorption peak at 597 mμ for QA and that at 430 mμ for QAQ. The actual per cent of QA or QAQ is calculated in terms of a known reference standard for each. A typical calculation for QA is as follows:

Calculations:

Let k = Extinction coefficient of solution of reference standard quinacridone

d = Optical density of solution of reference standard quinacridone

c = Concentration (grams/l.) of solution of reference standard quinacridone

l = path length in cm. of reference standard

k' = Extinction coefficient of solution of quinacridone sample

d' = Optical density of solution of quinacridone sample

c' = Concentration (grams/1.) of solution of quinacridone sample

l′=sample path length in cm.

$$(1)\ k=\frac{d}{c^1}$$

$$(2)\ k'=\frac{d'}{c'1'}$$

$$(3)\ \%QO=\frac{k'}{k}\times 100$$

The following Examples, in which all parts are by weight, are given by way of illustration only. Example 2 is included for the purpose of comparison.

EXAMPLE 1

Twenty parts of SNBS (0.089 mole) and 17.3 parts of SMA (0.089 mole) are added to a solution of 20 parts of sodium hydroxide in 113 parts of water. The mixture is stirred at 35—40°C. for 1 hour and then 10 parts (0.0318 mole) of unsubstituted 6,13-dihydroquinacridone is added and the mixture is heated gradually with stirring to reflux temperature. Refluxing is continued for 4 hours, after which 500 parts of water is added and the product is isolated by filtration, and washed free of soluble base. The product is then treated with 175 parts of concentrated hydrochloric acid and the mixture is refluxed for 1/2 hour. The product is isolated by filtration, washed free of soluble chloride ion and dried. It has a QAQ/QA ratio of 6.47.

While the infrared absorption spectrum of the original product isolated after the oxidation shows no absorption band at 430 mμ, which is typical of QAQ since the QAQ present at this point is in the form of the sodium salt of the enol isomer, after treatment of the product with hydrochloric acid and isolation, the infrared absorption spectrum shows a strong band at 430 mμ, indicating the presence of QAQ in the quinone form.

When the procedure of this example is repeated except that the SNBS is omitted, no perceptible oxidation of the unsubstituted 6,13-dihydroquinacridone occurs, even after 4 hours of refluxing. However, when the regular amount of SNBS is introduced into the reaction mixture, an immediate color change, indicating oxidation of the unsubstituted 6,13-dihydroquinacridone, takes place, this demonstrating that the SMA *per se* does not oxidize the unsubstituted 6,13-dihydroquinacridone and that a separate oxidant is necessary.

When the procedure of this example is repeated except that a reaction medium of 60 parts of water and 80 parts of methanol is used instead of 113 parts of water, a product having a QAQ/QA ratio of 0.66 is obtained. 100 parts of the 0.66 QAQ/QA product is milled and processed following the technique of Example 14 of U.S. Patent No. 3,160,510 to form a solid solution of the components. The dry pigment so formed is suspended in 1000 parts of dimethylformamide, heated at the boil under reflux for about 20 hours, cooled, filtered, washed free of solvent, and dried to give a maroon pigment of strength, lightfastness and x-ray diffraction pattern similar to that of the product of Example 15 of U.S. Patent No. 3,160,510.

When the procedure of this example is repeated except that 15.4 g of sulfanilic acid is substituted for the SMA, a product with a QAQ/QA ratio of 3.91 is obtained.

EXAMPLES 2—9

The procedure of Example 1 is followed except that the mol ratio of SNBS/SMA is varied as indicated, producing variation in the QAQ/QA ratio, as shown in the drawing and as reported in the Table.

TABLE

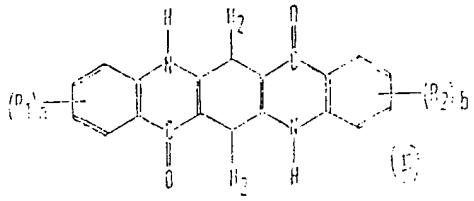
Example No.	SNBS/SMA (mole ratio)	QAQ/QA (weight ratio)
2	1/0	0.48
3	1/0.1	0.84
4	1/0.2	1.27
5	1/0.3	1.56
6	1/0.4	1.89
7	1/0.6	2.46
8	1/0.8	2.85
9	1/1.1	6.79

Total yields in the foregoing examples range from 81—94% of theory with the highest yields being obtained in those cases where the larger amount of SMA is used.

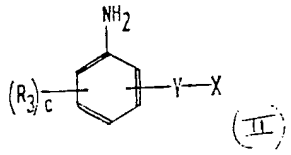
The product from Example 8 is ball milled with 900 parts of crystalline sodium chloride and subsequently processed as outlined in detail in Example 14 in U.S. Patent No. 3,160,510. The resulting product has an X-ray diffraction pattern corresponding to that found in the product of Example 14 of U.S. Patent No. 3,160,510. The similarity of this diffraction pattern to that of pure QAQ and the absence therefrom of any characteristic lines of linear quinacridone *per se* indicate that the final product is a solid solution of QA in QAQ. This reddish-yellow pigment is of interest because of its good intensity and lightfastness.

WHAT WE CLAIM IS:—

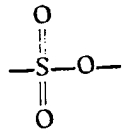
1. A process for preparing a mixture of a quinacridonequinone and a quinacridone which comprises oxidizing, in an alkaline medium, a corresponding dihydroquinacridone of the general formula



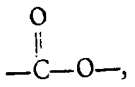
wherein R_1 and R_2, which may be the same or different, are a halogen atom, an alkyl group of from 1 to 3 carbon atoms, or an alkoxy group of from 1 to 3 carbon atoms, and *a* and *b*, which may be the same or different, are 0, 1, or 2, in the presence of a compound of the general formula:



wherein R_3 is as defined above, for R_1 and R_2, *c* is 0, 1, 2, 3, or 4, —Y— is the group



or



and —X is sodium or potassium.

2. A process according to Claim 1 wherein the compound of formula I is dihydroquinacridone and the compound of formula II is sodium metanilate.

3. A process according to Claim 1 or 2 wherein as oxidizing agent there is used nitrobenzene, sodium *m*-nitrobenzenesulfonate, *p*-nitrotoluene, *m*-nitrophenol, *p*-nitrobenzoic acid, *m*-nitrobenzoic acid, 4-nitrophthalic acid or sodium 2-methyl-5-nitrobenzenesulfonate.

4. A process according to Claim 2 wherein the oxidizing agent is sodium *m*-nitrobenzenesulfonate and wherein the mole ratio of said sodium *m*-nitrobenzene sulfonate to sodium metanilate is from 1/0.1 to 1/1.1.

5. A process according to Claim 1 wherein the compound of formula I is dihydroquinacridone and the compound of formula II is sodium sulfanilate.

6. A process for preparing a mixture of a quinacridonequinone and a quinacridone from a corresponding dihydroquinacridone substantially as described in any of Examples 1 or 3 to 9.

7. A mixture of a quinacridonequinone and a quinacridone when produced by the process claimed in any of Claims 1 to 6.

A. A. THORNTON & CO.,
Chartered Patent Agents,
Northumberland House,
303/306 High Holborn, London, W.C.1.

Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1971.
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.

1 SHEET

This drawing is a reproduction of the Original on a reduced scale